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Comparison of different types of diffusive gradient in thin film samplers for measurement of dissolved methylmercury in freshwaters

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ABSTRACT

Determination of bioavailable concentrations of methylmercury ($MeHg^+$) in freshwater is key to further understanding its potential risk and toxicity. In this work, two in-house-manufactured mercury-specific diffusive gradients in thin films (DGT) were used in laboratory to assess the lability of $MeHg^+$, and to develop a relationship between chemical lability and bioavailability. After diffusing through the diffusive gel, the $MeHg^+$ accumulated in a thiol functionalised resin gel was extracted using acidic thiourea that was analysed using aqueous-phase propylation followed by headspace solid-phase microextraction (HS-SPME) and gas chromatography (GC) coupled to pyrolysis-atomic fluorescence spectrometry (Py-AFS) detection. The diffusion coefficient (D) at 25 °C in agarose (A-DGT) in the absence and presence of dissolved organic matter (DOM) was obtained. Moreover, these values were experimentally compared against polyacrylamide (P-DGT), which is the most frequently used DGT for mercury to date. Statistically significant differences were observed between D values for A-DGT in the absence (3.15×10^{-6} cm^2 s^{-1}) and presence of DOM (2.68×10^{-6} cm^2 s^{-1}) and also for P-DGT (2.49×10^{-6} and 1.69×10^{-6} cm^2 s^{-1}). Interestingly, our results show that diffusion of $MeHg^+$ was higher on agarose diffusive gel with and without DOM in comparison with those observed in polyacrylamide. Even with higher diffusion coefficients of $MeHg^+$ in the agarose diffusion layer, however, DGT based on polyacrylamide seems to be a better choice for eutrophic waters, when monitoring very low concentrations of $MeHg^+$, considering its slightly higher uptake capacity.

1. Introduction

Among mercury (Hg) species occurring in the environment, methylmercury ($MeHg^+$) is identified as one of the most critical regarding its biotic effects. The reason for this is that it is a potent neurotoxin that has the ability to pass through biological membranes, low metabolism and excretion rates and, consequently, can bioaccumulate and biomagnify throughout aquatic trophic chains [1,2].

Since contamination by mercury in aquatic ecosystems is of great concern, monitoring of its species has attracted special attention. In freshwater environments, both inorganic and organic (e.g. $MeHg^+$) mercury can be partitioned between suspended particulate matter (SPM), dissolved and to colloidal water phases. The latter is associated with the DOM occurring in freshwater ecosystems [3,4]. This influences the speciation and potentially the bioavailability (i.e. its availability to be taken up by biota) of mercury [5]. Determining the bioavailability of $MeHg^+$ is also essential in order to assess its risk and potential effects on exposed biota. For this purpose, the diffusive gradients in thin films (DGT) technique can be used. This technique was developed in 1994 [6] for in situ determination of kinetically labile metal species in aquatic systems. The principle of the DGT technique is based on the diffusion of the dissolved species through a membrane-diffusive layer and their accumulation in an ion-exchange resin. A hydrogel and a membrane filter are commonly used as the diffusive layer and the resin is incorporated into a polyacrylamide gel. These three layers are enclosed and sealed in a small plastic device, so that only the membrane is exposed to the deployed solution. The time-average concentration of metal in the solution, C, can be calculated with the help of Fick's first law of diffusion as follows:

$$C = \frac{M\Delta g}{DAt} \quad (1)$$

where D is the diffusion coefficient of the metal in the diffusive layer, t is the deployment time, A is the exposure surface area, and Δg is the thickness of the gel layer. The mass of the analyte accumulated by the resin is experimentally measured and the absolute mass M then provides the average labile metal concentration during the exposure time.

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In this work, in-house-manufactured DGT devices based on agarose and polyacrylamide diffusive gel were laboratory tested for the determination of the dissolved-bioavailable fraction of $MeHg^+$ in water. Time series experiments using an $MeHg^+$ solution, both with and without dissolved organic matter (DOM), were successfully carried out under controlled laboratory conditions.

2. Experimental

2.1. Gels preparation and DGT assembly

Two in-house-manufactured DGT devices were used. Both had 3-mercaptopropyl functionalised silica gel embedded in a polyacrylamide gel as the binding agent, but one of them had a 0.76 mm thick agarose gel (A-DGT) and the other had a 0.40 mm thick polyacrylamide gel (P-DGT) as the diffusive layer. In the two types a 0.1 mm thick 0.45 μm pore size nylon filter membrane was used on top of the diffusive gel. A procedure [7] used before was followed for preparing P-DGT, where the diffusive gel was made with polyacrylamide gel comprising 15% acrylamide (v/v) and 0.3% cross-linker (v/v). On the other hand, the agarose gels were prepared following a previous procedure [8]. A diffusive gel containing 1.5% agarose was prepared by dissolving the agarose in an appropriate volume of 80 °C warm deionised water. The mixture was placed in a boiling water bath and smoothly stirred until all the agarose was dissolved and the solution became transparent. This hot gel solution was immediately pipetted between two preheated glass plates separated by 0.76 mm plastic spacers and left to cool down to its gelling temperature (36 °C or below). The gel sheet was cut in discs immediately afterwards, since it would not expand (the expansion factor of agarose gel is 1) [9], and the discs were stored in Milli-Q water.

In both cases, the binding layer, also known as the resin gel, consisted of a 3-mercaptopropyl functionalised silica gel (Aldrich) embedded in a polyacrylamide gel. A piston type plastic moulding (DGT Research Ltd, UK) was used to support the gels and to ensure that only a known surface of the DGT unit (area = 3.14 cm^2) was in contact with the solution. It consisted of a backing cylinder and a front cap with a 2 cm diameter window. Gels and a filter were placed on top of the cylinder. A 0.4 mm thick resin gel disk was placed on top of the cylindrical piston, with the side containing the gravity-deposited resin beads facing upward and was used to accumulate diffused methylmercury. On top of the resin gel was placed a 0.4 mm thick disk of diffusive gel (i.e. polyacrylamide). Finally, 0.1 mm thick nylon filter membrane (0.45 μm pore size) was placed on top of the diffusive gel for protection. The front cap was pressed down tightly, ensuring a good seal at the filter surface.

2.2. Reagents and materials

The reagents and materials employed for the preparation of the DGT gels [10] and for $MeHg^+$ determination [11] are described in previous works. Thiourea (ACS, ≥ 99.0%), purchased from Fluka (Steinheim, Germany) and HCl fuming 37% (ACS, ISO), purchased from Merck (Germany), were used to prepare an acidic thiourea solution for $MeHg^+$ elution from resin gels. Methylmercury chloride (CH_3HgCl, 99%) was obtained from Strem (Newburgport, MA, USA), and dimethylmercury chloride (CH_3CH_2HgCl) from Alfa Aesar (Karlsruhe, Germany). Stock standard solutions were prepared at 1000 mg L^{-1} (as Hg) in acetone and stored at −20 °C. Working solutions were prepared weekly by diluting the stock solutions with acetone to a range of 0.02–500 μg L^{-1} (as Hg).

2.3. Apparatus

Gas chromatography coupled to atomic fluorescence spectrometry via a pyrolytic reactor (GC-Py-AFS) was used for the analysis of $MeHg^+$ in water samples and DGT resin gel eluates. The GC analysis was accomplished with a non-commercial system formed by a Thermo Trace GC ultra (Milan, Italy) gas chromatograph interfaced to an AFS Tekran Model 2500 (Toronto, Canada) detector via pyrolyzer (Hg-800, Rektorik R&D Chromatography, Meyrin, Switzerland). Details of GC analysis have been outlined previously [11].

2.4. Calibration of DGT units for $MeHg^+$ measurements

Two $MeHg^+$ solutions (1 μg L^{-1} MeHgCl, 0.01 M NaCl), one with organic matter from a Nordic Reservoir (IHSS, 1R108N) (10 mg L^{-1}) and the other one without it, were prepared in 5 L amber glass bottles. The pH was adjusted to 7 using NaOH (2 M) or HCl (0.5 M). Afterwards, the solution was left to equilibrate overnight while being stirred with a magnetic stirring bar. Ten DGT devices of each type (i.e., A-DGT and P-DGT) were submerged in each solution, whose temperature was controlled and kept at 25 ± 0.5 °C. Duplicates of DGT units were retrieved after 2, 4, 8, 14 and 24 h. A duplicate not deployed was considered as DGT blank (0 h). At each sampling interval, 5 mL of each $MeHg^+$ solution were collected and acidified to 0.4% with HCl to monitor the $MeHg^+$ concentration remaining in solution, and 10 mL was taken only from the DOM containing solution to measure DOC. Both the DGT units and the water samples were stored in the fridge until analysis.

2.5. Elution of $MeHg^+$ from DGT resin gels

After being retrieved from the DGT assembly, every resin gel was placed in a glass vial using hydrochloric acid (10%) cleaned tweezers. 2 mL of a freshly prepared acidic thiourea solution (1.3 mM thiourea, 0.1 M HCl) was added to each vial, which was wrapped with aluminium foil to prevent photodegradation and left at room temperature for the elution to take place. Following 24 h of exposure period, the vials were stored in the fridge (4 °C) until analysis (within a week).

2.6. $MeHg^+$ determination and quality assurance

$MeHg^+$ was measured as previously described elsewhere [11] with some modifications. Briefly, a 250 μL aliquot of resin extract was placed in a 6 mL glass vial with PTFE-coated silicone rubber septum containing 3 mL of citric-citrate buffer (pH = 4.5–5). 10 μL of EtHgCl (230 pg mL^{-1} as Hg) in acetone was also added to the vial as instrumental standard and 100 μL of 1% $NaBPh_4$ aqueous solution was added as derivatising agent. After a 5-min derivatisation step, extraction was accomplished for 27 min by headspace solid-phase microextraction (HS-SPME) using a 100 μm PDMS fibre. The final detection was carried out using a GC-Py-AFS. Three resin gels were spiked with 3 ng of $MeHg^+$ in order to calculate the recovery of the method, which was 65% (RSD = 4%, n = 3). This value was later used to correct the results. In the case of the water samples, the methodology had two differences: the EtHgCl was added as internal standard right after taking the samples and before storing them to correct for any possible loss of $MeHg^+$ during storage or due to adsorption on the vial walls, apart from detector variations; the aliquot of sample for HS-SPME was 1 mL.

The repeatability, expressed as relative standard deviation (RSD), was evaluated every time the instrument was switched on to run a set of samples by applying the proposed method to the same sample. Results (RSD < 5%, n = 3) reveal the robustness of the

analytical procedure. A six-point calibration curve was performed in the range from 29 to 1180 pg of $MeHg^+$ (as Hg). The limit of detection (LOD) was calculated as the mean of the method blanks plus 3 times their standard deviation, and the limit of quantification (LOQ) as the mean of the method blanks plus 10 times their standard deviation, resulting in 5.8 and 19 pg, respectively.

2.7. Statistical analysis

Since the diffusion coefficient was calculated from the slope of the relationship between the mass of $MeHg^+$ accumulated by the DGT units and the deployment time [12], we tested whether there is any significant difference in the slopes using a two-sample *t*-test. The significance level was set at $p \leq 0.01$. Statistical analysis was performed using the IBM SPSS Statistics 19 (SPSS Inc., Chicago, IL, USA).

3. Results and discussion

DGT devices have been calibrated with and without DOM to better simulate natural water conditions in the field. The results of these calibration experiments showed that both DGT types in the presence and the absence of DOM proportionally accumulate $MeHg^+$ in relation to exposure time, as evidenced by the regression coefficients of the four linear curves ($R^2 > 0.99$) (Fig. 1). In any case, the results of time-series experiments confirm the validity of the basic DGT principles as was proved previously [10].

The diffusion coefficient (D) of $MeHg^+$ in the diffusive layer can be calculated from the slope of the relationship between the mass of $MeHg^+$ accumulated by the DGT units and the deployment time [12] (Fig. 1). When the analyte concentration in the solution varies, the mass accumulated in the DGT resin gel should be normalised for it. However, in our experimental conditions, as we worked with quite a high volume of solution, then $MeHg^+$ concentration barely decreased because of DGT uptake. In A-DGT, the diffusion coefficient of $MeHg^+$ in the diffusive layer in the absence (nDOM, D^+_{MeHg}) and presence of DOM ($D^+_{MeHg\ -DOM}$) was 3.15 (± 0.06) $\times 10^{-6}$ and 2.68 (± 0.05) $\times 10^{-6}$ $cm^2\ s^{-1}$, respectively, at 25 °C; however, in P-DGT it was 2.49 (± 0.04) $\times 10^{-6}$ and 1.69 (± 0.05) $\times 10^{-6}$ $cm^2\ s^{-1}$, respectively, at 25 °C (Table 1). All of the diffusion coefficients were significantly different from each other ($p < 0.01$). These results show that the agarose-based DGT is able to successfully measure $MeHg^+$ in freshwater with DOM, with similar results as polyacrylamide, which is nowadays the most commonly used diffusive gel in DGT for mercury. In fact, diffusion coefficients values in agarose are higher than in polyacrylamide gel, especially in the presence of DOM (about 60% higher), which seems to mean that agarose gel improves the uptake of $MeHg^+$ in both conditions. Nevertheless, this is not completely true since P-DGT is able to obtain more $MeHg^+$ per unit of time than A-DGT. In fact, diffusivities for $MeHg^+$ in agarose gel are higher, but its uptake by P-DGT is higher than for A-DGT (e.g. according to Fig. 1, in 24 h, P-DGT gets 9.2 ng whereas A-DGT adsorbs 8.5 ng). Moreover, if monitoring very low Hg concentrations in eutrophic waters, P-DGT seems to be the best choice, considering its slightly higher uptake capacity. The eutrophic waters promote algal growth and, consequently, biofouling phenomena; therefore, these results demonstrate that P-DGT may uptake $MeHg^+$ faster than A-DGT, reducing the probability of biofilm growth before uptake begins.

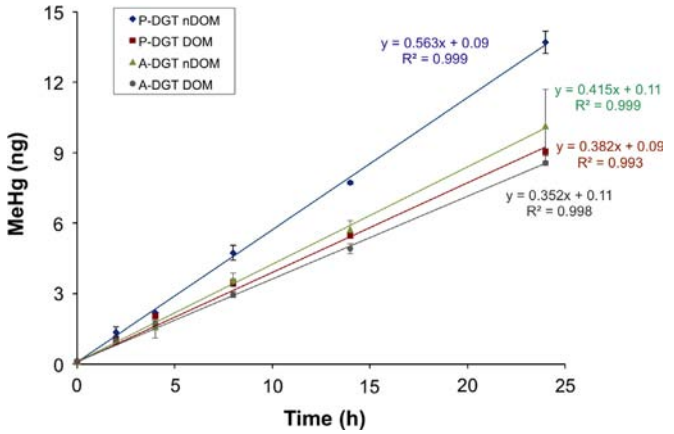

Fig. 1. Time-series experiment. Mass of methylmercury accumulated in the resin at different deployment times for the two DGT types (A-DGT and P-DGT), both in the absence (nDOM) and in the presence of DOM.

Table 1
Diffusion coefficients ($\pm$ SE) of $MeHg^+$ in the absence (nDOM) and in the presence of DOM at different temperatures.

	$D^+_{MeHg} \times 10^{-6}$ ($cm^2\ s^{-1}$)				
	25 °C		20 °C		
	nDOM	DOM	nDOM	DOM	
A-DGT	3.15 ± 0.06	2.68 ± 0.05	2.74 ± 0.06[a]	2.33 ± 0.05[a]	This study
	5.26 ± 0.39[b]	3.57 ± 0.29[c]	nc	nc	[15]
P-DGT	2.49 ± 0.04	1.69 ± 0.05	2.17 ± 0.04[a]	1.47 ± 0.05[a]	This study
	nc	nc	5.1 ± 0.3	nc	[7]
	nc	nc	nc	0.7	[17]

[a] Data obtained from 25 °C after temperature correction made by Eq. (2).
[b] Diffusive layer thickness is 0.75 mm in 0.1 M NaCl, pH 7.7.
[c] Overall diffusion coefficient obtained under different thicknesses (0.5, 0.75 and 1.0 mm) in 0.1 M $NaNO_3$, 10 mg L^{-1} DOC, pH 7.3.

As expected, the diffusion coefficient of $MeHg^+$ in DOM was lower than that observed in the absence of DOM, and the values were consistent with the literature reported values of DOM diffusion coefficients. Diffusion coefficients of the Norwegian Natural organic matter in water ranged between 2.1×10^{-6} $cm^2\ s^{-1}$ and 3.0×10^{-6} $cm^2\ s^{-1}$ [13] and our measurements were similar. In another study, [14] the diffusion coefficients of humic and fulvic acids in agarose layer were 1.19×10^{-6} $cm^2\ s^{-1}$ and 1.92×10^{-6} $cm^2\ s^{-1}$ at 20 °C, respectively, which are in the range of our measurements at 25 °C and converted values at 20 °C (see Table 1).

In the agarose layer, the observed diffusion coefficient of $MeHg^+$ in DOM was close to that reported by Hong et al. [15], $D_{MeHg^+\ -DOM}$: 3.82 (± 0.16) $\times 10^{-6}$ $cm^2\ s^{-1}$ in comparable agarose layer thickness (0.75 mm). However in the absence of DOM the diffusion coefficient in agarose was slightly lower than the reported diffusivity of 5.26 (± 0.39) $\times 10^{-6}$ $cm^2\ s^{-1}$ [15].

In order to compare D values with other studies, the diffusion coefficient at any temperature, D_T, can be calculated by applying Eq. (2) [16], where D_{25} is the diffusion coefficient of ions in water at 25 °C:

$$\log D_T = \left(\frac{1.37(T-25)+8.36 \times 10^{-4}(T-25)^2}{109+T}\right) + \log\left(D_{25}\left(\frac{273+T}{298}\right)\right) \quad (2)$$

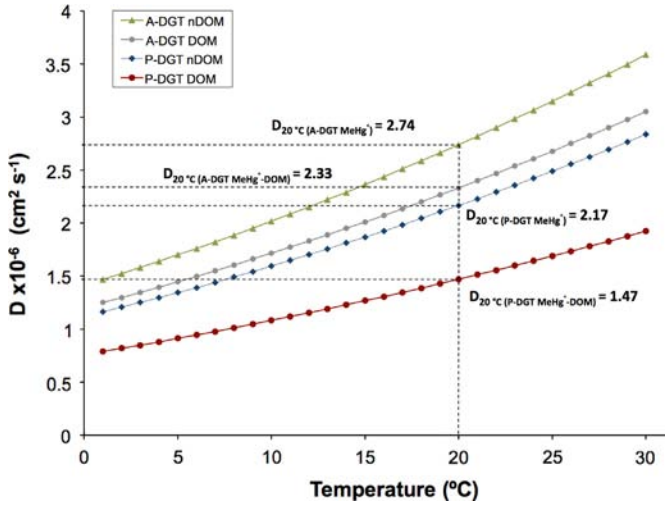

Fig. 2. Diffusion coefficient of $MeHg^+$ in the two different diffusive layers (A-DGT and P-DGT) in the absence (nDOM) and in the presence of DOM, calculated on the base of Fick's law for a wide range of temperatures.

Consequently, along with our *D* values obtained at 25 °C, our recalculated values at 20 °C (Fig. 2) and previous measurements of diffusion coefficients for agarose and polyacrylamide reported by Hong et al. [15] and Clarisse studies [7,17] are shown in Table 1 for comparison.

As observed in Table 1, our recalculated value in the absence of DOM is lower compared with data from [7], whereas in the presence of DOM it is higher versus data from [17], although experiments were performed in similar conditions. In fact, in experiments performed in the absence of DOM, there are no differences between both ionic strengths solutions prepared with NaCl (0.1 M vs. 0.01 M), since according to the DGT theory, uptake rates are independent of ionic strength [16], as long as it is higher than 1 mM [18], which is the case here. Moreover, Hong et al. [15] reported that there is a negligible ionic strength effect in the performance of DGT probes when Hg species were complexed with chloride. Apart from that, concerning experiments in DOM, $D^{+}_{MeHg\ -DOM}$ was determined by submerging the DGT units in a 10 mg L^{-1} DOC solution, whereas Clarisse et al. [17] performed their experiment in a solution of $MeHg^+$ saturated with DOM. In both cases, the same organic matter, i.e. Nordic Reservoir NOM (IHSS, 1R108N), was employed. This provides proof of the importance of calibrating the DGT units in a solution with similar characteristics to those of the water in which DGT will be deployed. Moreover, our D^{+}_{MeHg} is similar to the diffusion coefficients of fulvic acid in polyacrylamide gel (1.15×10^{-6} cm^2 s^{-1}) reported by Zhang and Davison [14].

In the case of A-DGT, another finding of interest was obtained since diffusion coefficients of $MeHg^+$ with and without DOM showed significant differences ($p<0.01$). On the other hand, the diffusion coefficients of Hg^{2+} obtained previously by Cristal et al. [10] with DOM (0.80×10^{-6} cm^2 s^{-1}) and without DOM (3.52×10^{-6} cm^2 s^{-1}) are also statistically significant ($p<0.01$). Although a significant difference was found in both cases, *D* values are very similar between them for $MeHg^+$ species in the presence or absence of DOM (D_{MeHg^+}: D_{MeHg^+}- DOM = 1.2), whereas for Hg^{2+} it is an order of magnitude higher with no DOM. The fact that the presence of DOM in solution did not decrease the *D* in the case of $MeHg^+$ as much as in the case of Hg(II) ($D_{Hg(II)} \approx 4.4\ D_{Hg(II)-DOM}$) suggests that $MeHg^+$–DOM complexes are more labile than Hg(II)–DOM complexes. Similar behaviour was observed for P-DGT, with significantly different *D* values between inorganic Hg in the absence and/or presence of DOM [10] in front of diffusion coefficients of organic species that also showed significant differences.

$MeHg^+$ tends to more strongly associate with humic acid, which has bigger sizes and slower diffusion coefficients, than fulvic acid [19]. Therefore the obtained higher (and faster) diffusion coefficient for $MeHg^+$ compared with Hg^{2+} should be related to the association of $MeHg^+$ to the smaller sized fulvic acids or due to its higher lability [20]. The latter reason would be expected since $MeHg^+$ is considered to have a lower affinity for the thiol functional groups in organic matter than Hg^{2+} because the methyl functional group reduces its affinity to thiols. This implies that $MeHg^+$–DOM complexes are more labile than Hg^{2+}–DOM complexes and have a higher dissociation rate constant [15,21]. This faster diffusivity ($D^{+}_{MeHg\ -DOM}$) possibly indicates that the $MeHg^+$–DOM complexes were dissociating in the diffusion layer, and later the free $MeHg^+$ moves within the diffusion layer with effective diffusion coefficients of 3.15×10^{-6} cm^2 s^{-1} and 2.49×10^{-6} cm^2 s^{-1} for agarose and polyacrylamide, respectively.

This observation was consistent with a previous study [15] that was further supported by the differences in the effective diffusion coefficients observed under different thicknesses. The diffusion coefficients tended to increase by increasing the diffusion layer thickness. A thicker diffusion layer means a longer residence time for Hg–DOM complexes in the layer, which can allow for the dissociation of the complexes. On the other hand, it was also demonstrated that Hg sorption to the resin layer is not kinetically limited [15]. Moreover, since agarose layer is thicker than polyacrylamide, diffusion coefficients were higher, even with slightly lower sorption during the same deployment time.

4. Conclusions

From our findings, we showed that calibrating the DGT units in a solution with similar characteristics (i.e. quantity and quality of DOM) to those of the water in which the devices will be deployed for the measurement of $MeHg^+$ is almost mandatory. In the presence of DOM, diffusion coefficients of $MeHg^+$ between A-DGT and P-DGT were significantly different, whereas agarose values were higher than in polyacrylamide gels. Interestingly, this indicates that the DGT technique employing agarose might perform fairly well in waters dominated by DOM. Moreover, considering its slightly larger uptake capacity, when monitoring very low Hg concentrations in eutrophic waters, P-DGT seems to be the best choice. There are significant differences between the *D* values of $MeHg^+$ in both agarose and polyacrylamide diffusive gels, and the difference between *D* values with and without DOM was bigger for P-DGT than for A-DGT. This may suggest that P-DGT is more appropriate for measuring $MeHg^+$ since it discriminates better between free $MeHg^+$ ions and/or $MeHg^+$–DOM complexes. Future works should be focused on studying the influence of the type (quality) of DOM (i.e. humic and fulvic) present in the water on the bioavailability of $MeHg^+$.

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